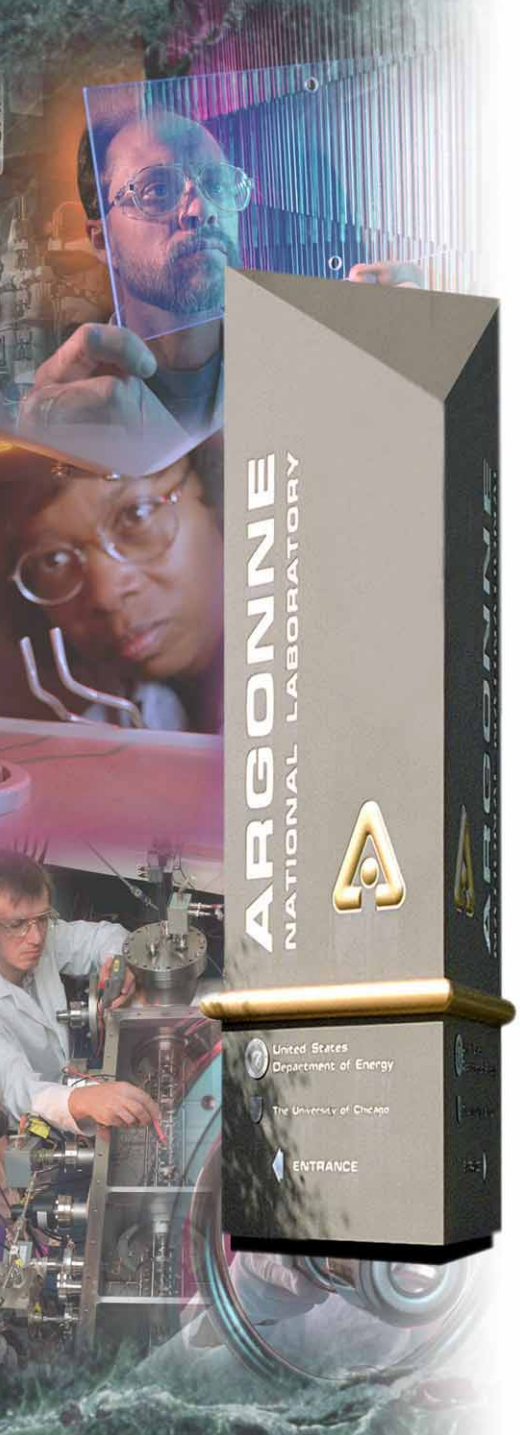

Development of Ultrananocrystalline Diamond (UNCD) Coatings

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Energy Systems Division

John A. Carlisle
Materials Science Division & Center for Nanoscale Materials

Argonne National Laboratory

Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

Project Goal

- **Develop applications for UNCD to achieve significant energy savings in IOF industries**
  - Focus on first application:
    - *Development of UNCD Coatings for SiC multipurpose mechanical pump seals*

Participants

- **Argonne National Laboratory**
  - John Hryn
  - John Carlisle
  - Dieter Gruen
  - Orlando Auciello
  - Michael Pellin
  - Ali Erdemir
  - Greg Krumdick
  - Jeff Elam
- **Industry Partners**
  - Advanced Diamond Technologies
  - John Crane, Inc.
  - Flowserve
  - Morgan AM&T
  - Coorstek Amazing Solutions
  - Innovative Plasma Systems GmbH (IPLAS)
- **University Collaborators**
  - Northwestern University
  - University of Illinois at Chicago

Technical Merit

- **UNCD addresses IMF Core Research Areas**
  - Wear, erosion, and corrosion resistance
    - *UNCD is low friction, chemically inert, hard as natural diamond*
  - Processing-properties relationships
    - *Development of large-areas plasmas, processing techniques*
  - Materials for sensors
    - *Electrochemical and UNCD MEMS-based (automotive, biomedical)*
  - Materials chemistry
    - *Novel Ar/CH_4 plasmas, C_2-dimer diamond growth*
  - Surfaces, interfaces, and joining
    - *Optimization of film adhesion, MEMS material integration*

Project Objectives

- **Develop fundamental understanding of UNCD growth processes**
  - Microwave plasma CVD process
  - Seeding of substrates
- **Develop a technological base for UNCD applications**
- **Demonstrate UNCD coatings in industrial applications**
  - SiC seal coatings for multipurpose mechanical pumps
  - Electrochemical sensors, MEMS, extrusion dies, etc.

Technical Progress

- **Delamination issue resolved**
  - Related to initial surface roughness
- **Seeding process optimized**
- **Simultaneous coating of multiple seals**
  - Critical for commercialization plan
- **Successful coatings of various substrates**
  - alpha-SiC, WC, CDC (chlorination of SiC)
- **Coated seals characterized and tested in pumps at Argonne and at industry partners**

Technical Outlook

- **Plan:**
  - Coat multiple seals simultaneously in large IPLAS reactor, measure waviness, meet spec.
    - *Resolve issue of carbon nanotube growth on SiC*
  - Testing of seals by industrial partners in high-value-added application
    - *High pressure, dry, hard-on-hard conditions*
    - *Quantify energy, economic benefits*
  - Field tests by customers of industrial partners (end-users) in IOF industries

Market Potential

- **1,000,000 chemical process pumps in U.S.**
  - Assuming 80% market penetration
- **Initial introduction to chemical pump seals**
  - High-value, high-performance application
- **Move to multipurpose and automotive pump applications in many IOFs**
  - Main competition is in uncoated SiC seals

Commercialization

- **Advanced Diamond Technologies**
  - Argonne-initiated start-up company
  - Business plan established
  - Toll processor for seal manufacturers
    - *Agreements in principle reached with partners*
- **Commercial demonstration of UNCD coating on SiC seals at ADT: 3-4 years**
  - Subject to available resources
    - *Investors, stakeholders, DOE-IOF teams*

Benefits (as SiC seal coating)

- **1,000,000 chemical process pumps in U.S.**
  - Assuming 80% market penetration
- **20% energy savings – lower friction losses**
  - Six-fold decrease in pump shaft torque
  - 236 trillion Btu savings cumulative by 2020
- **Substantial economic benefit**
  - $3.5 billion savings cumulative by 2020
- **Environmental benefits**
  - 4,700,000 TCE reduction cumulative by 2020

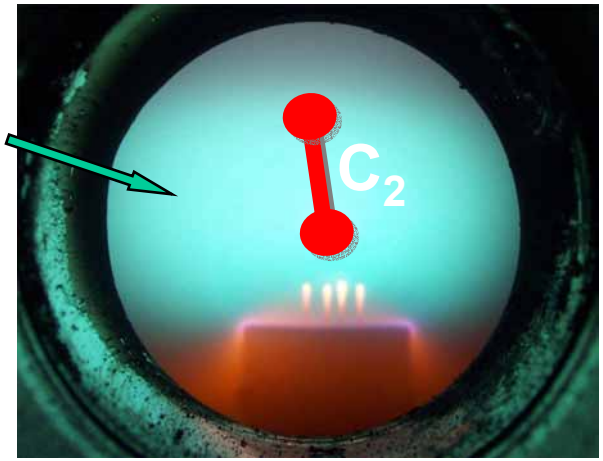
Technical Summary

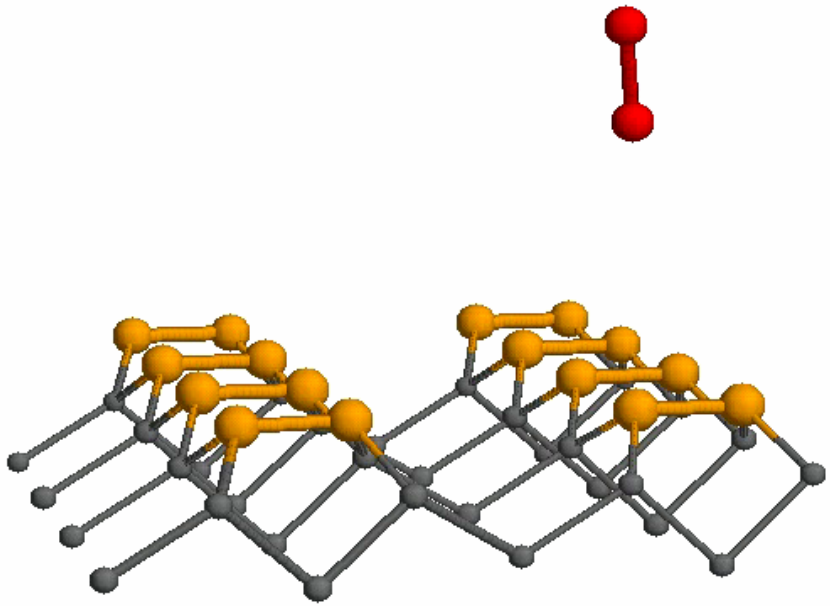
- **Delamination issue resolved for 3” reaction-bonded seals**
  - 3” Seals extensively tested in test pump at ANL
  - Films that don’t delaminate don’t wear out (so far)
- **Coating of multiple seals demonstrated**
- **Coating of different types of seal demonstrated**
  - Reaction bonded SiC, sintered α-SiC, WC
  - 1” automotive, 2” & 3” engineered seals
- **Carbide-derived carbon facility designed, built, commissioned**
  - UNCD successfully grown on CDC-treated SiC seal
- **Rotating Seal Manipulator installed and commissioned**

Ultrananocrystalline Diamond

Microwave Plasma CVD

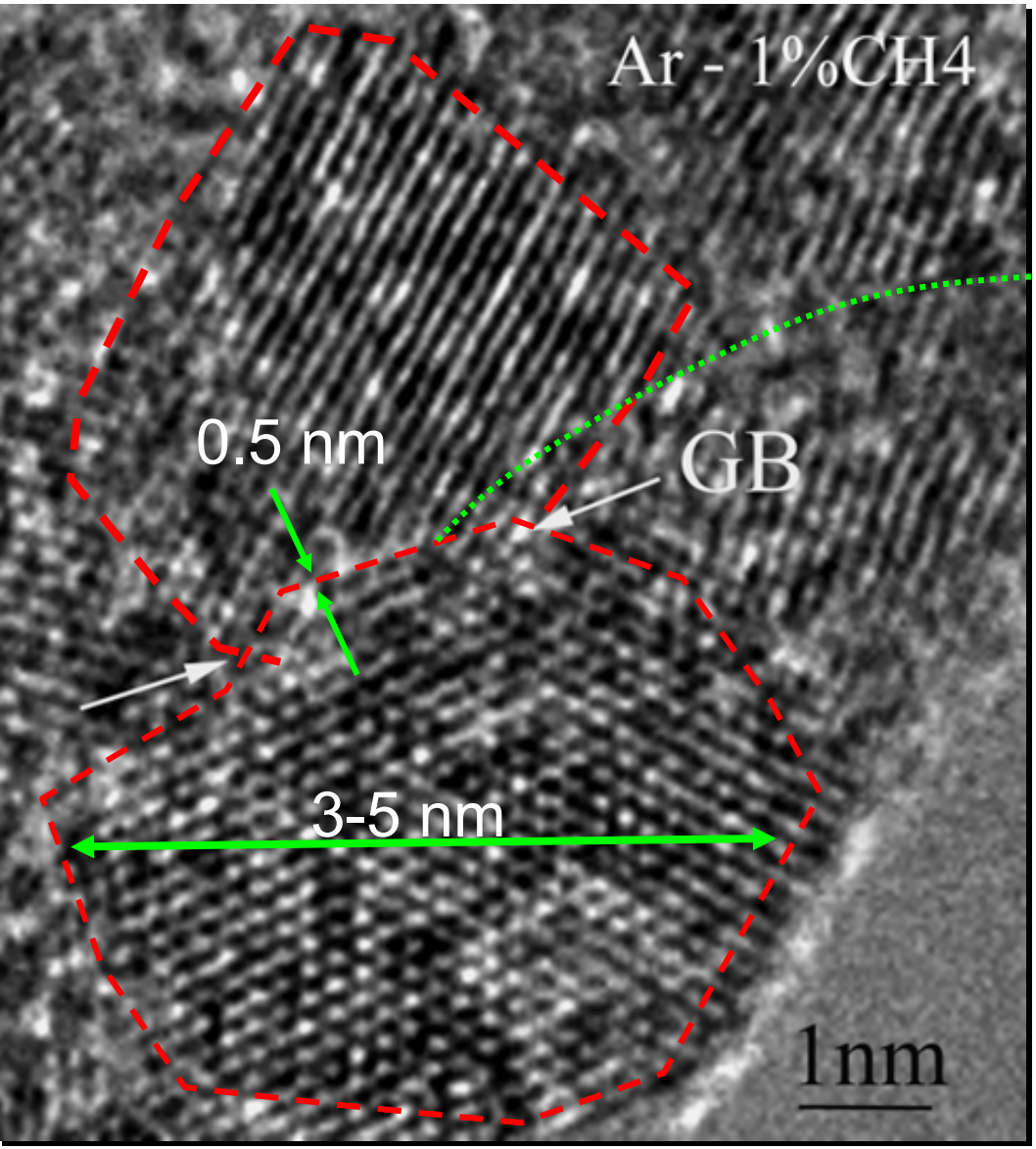
Ar/CH_4 plasma

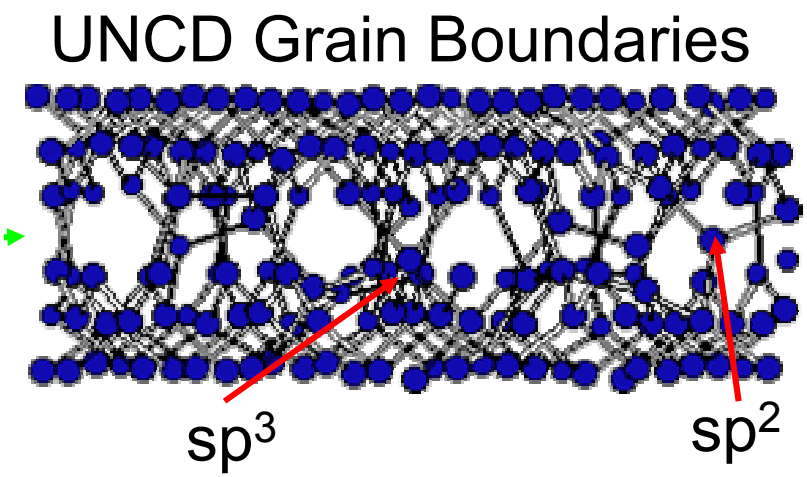




- C_2 Dimers will naturally form diamond-bonded carbon (sp^3-bonded)
- Hard has natural diamond (97 GPa), Young's Modulas ~980 GPa
- Tougher that microcrystalline diamond (fracture strength ~4 GPa)
- Smooth, low friction as deposited (~20 nm rms)

Nanoscale Structure of UNCD





- **3-5 nm Grains**
- **High-Energy Grain Boundaries**
- **UNCD isn't pure diamond**
  - *Self-assembled Nanocomposite* of diamond and graphite

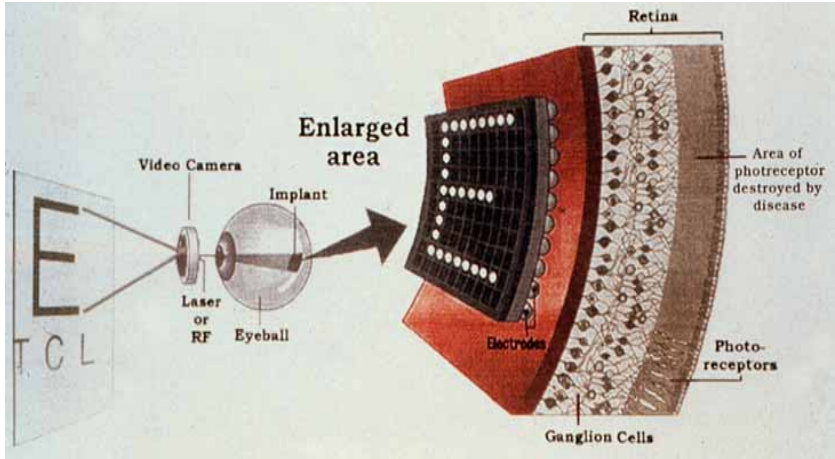
New iplas Microwave Plasma System

- New Plasma Chemistries
  - B, Al, P, etc.
- Higher Pressures
  - Faster deposition (~.5 µm/hr)
- Larger Area
  - 100 mm wafers, UNCD-MEMS
  - 2” RO SiC Pump Seals
  - Scalable!

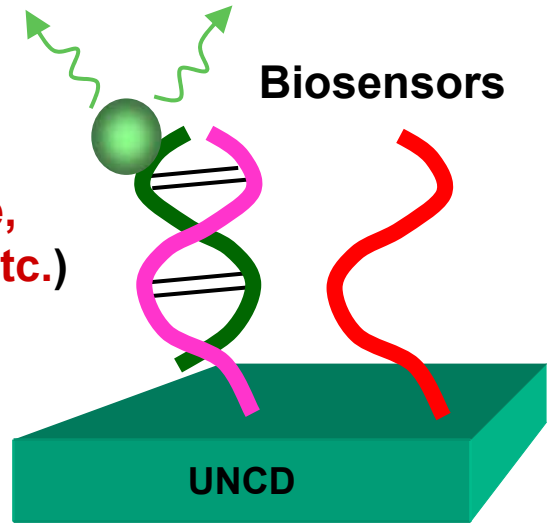
Current Work & Industrial Collaborations

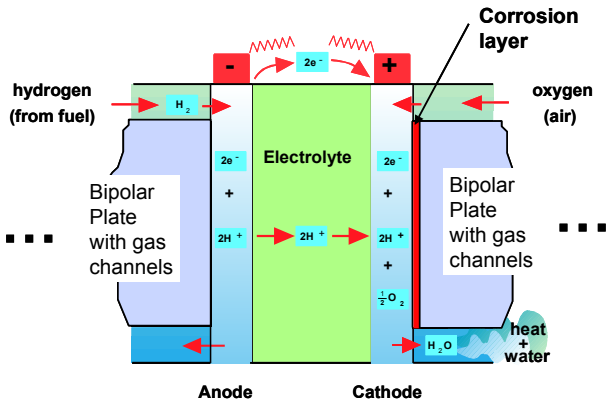
New MPCVD Reactor (iplas)

Artificial Retinas (Second Sight)

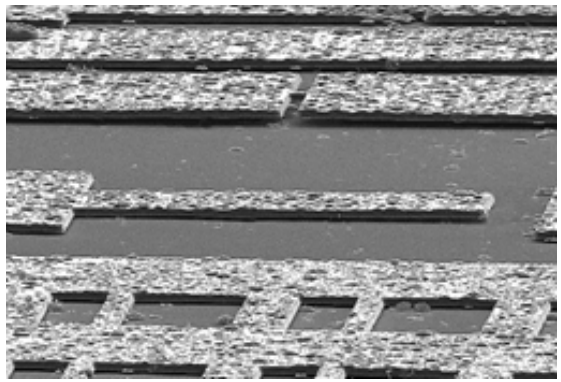


Tribo-mechanical Coatings (John Crane, CoorsTek, etc.)



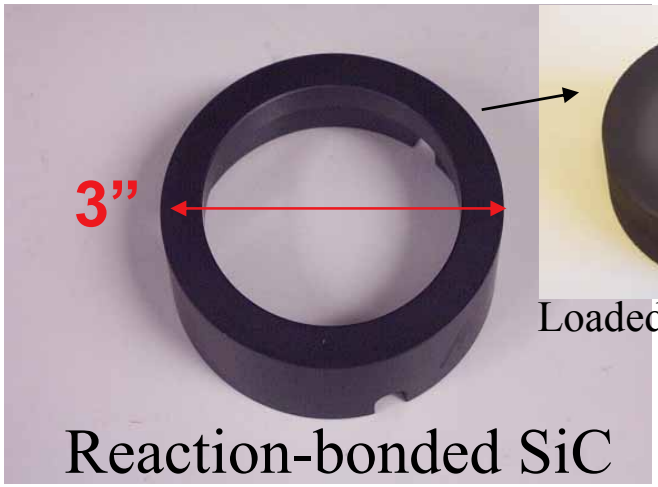


Fuel Cells (Delphi Auto.)



UNCD MEMS (Motorola, Intel, …)

3” reaction-bonded SiC Chemical Pump Seals

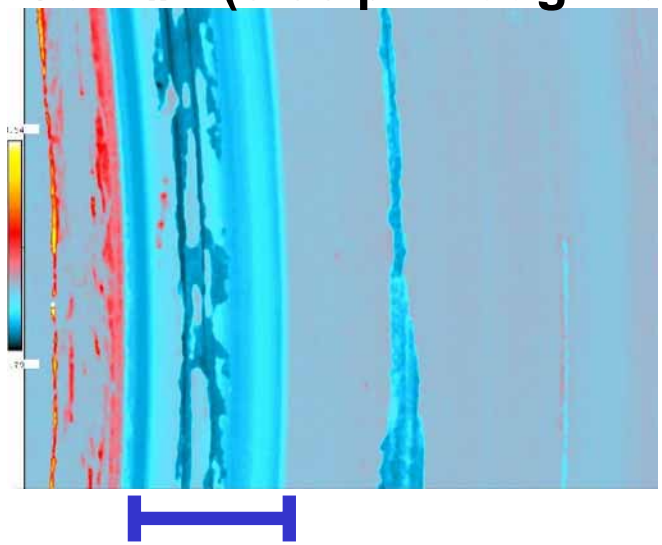


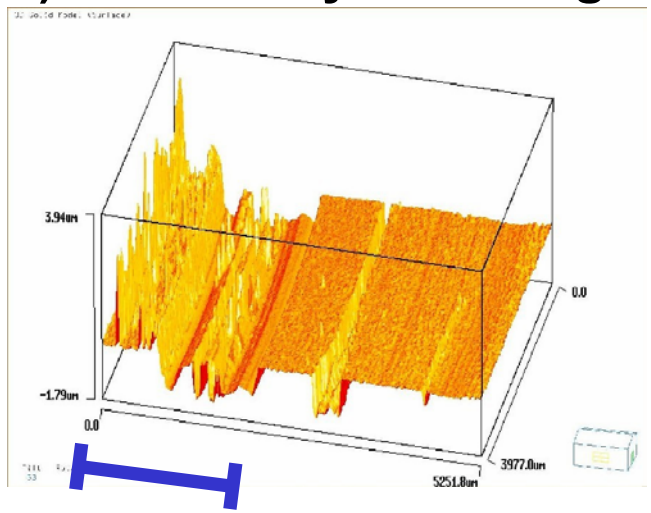
- **Milestone**
  - Coat larger 3” SiC seals
  - Solve delamination problem
- **3” reaction bonded SiC seals were pretreated to have different surface roughnesses**
- **Seals were coated with ~1 mm UNCD films using 4 hour process at 850°C**
- **optical profilometry and Raman spectroscopy performed before and after wear-testing**

- **Seals are tested in pairs: coated and uncoated**
- **Each seal rotates against a graphite counterface at 3000 RPM**
- **After run-in period, pressure = 100 PSI**
- **Each day, fixture is disassembled and seals are inspected for wear**

Profilometry of 3” seals after testing

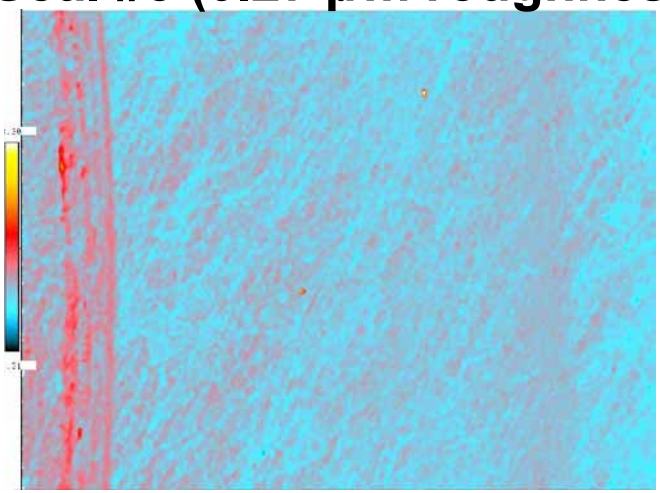
Seal #2 (0.06 µm roughness) after 1 day of testing

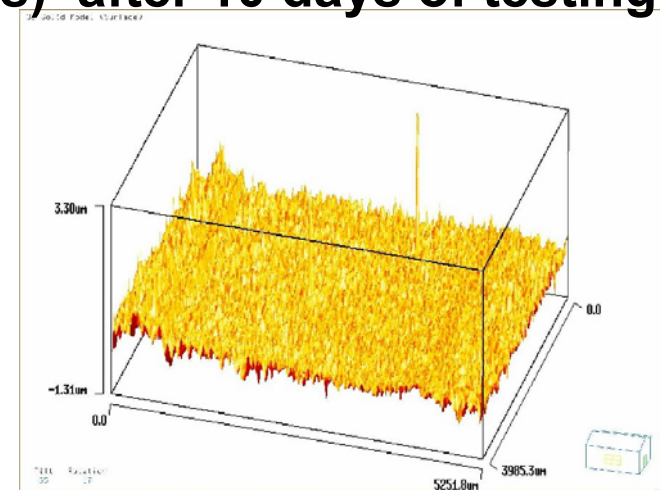




- Severe delamination observed at areas contacting graphite counterface

Seal #5 (0.27 µm roughness) after 10 days of testing



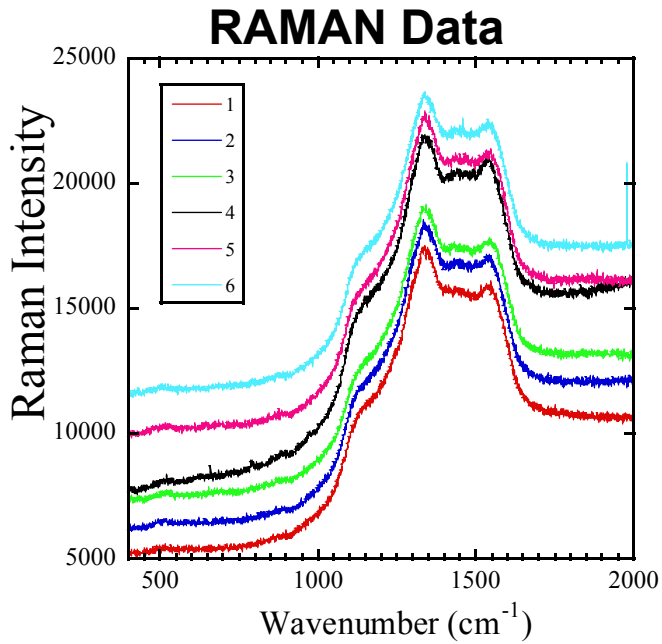


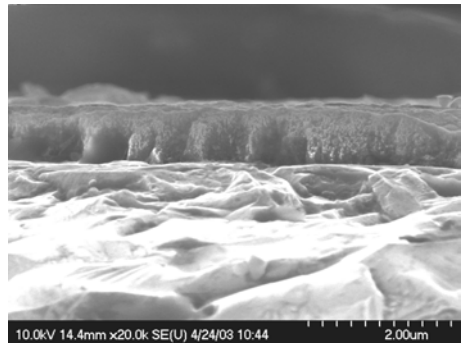
- NO Delamination!

Compare coated versus uncoated seals

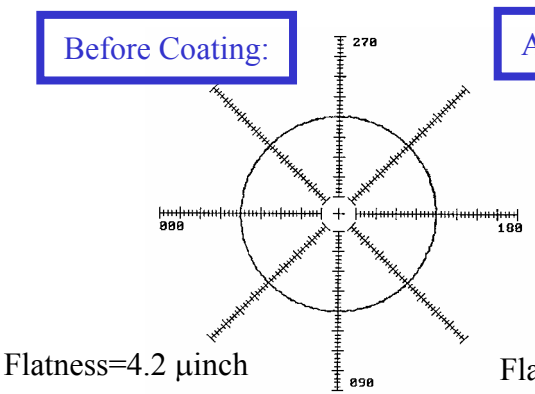
- **High initial surface roughness critically improves UNCD adhesion**
- **UNCD films that don't fail dramatically improve seal lifetime**
- **Torque reduced by factor of 6**
  - 20% energy savings

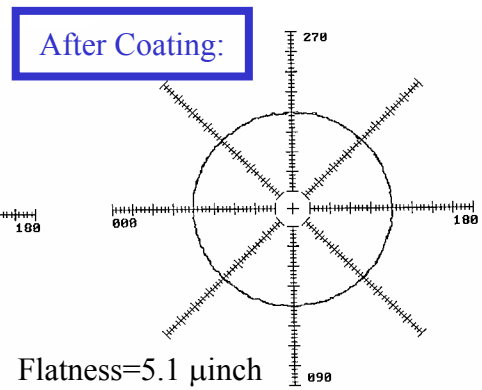
α-SiC automotive seals





Cross-section SEM of UNCD film on seal

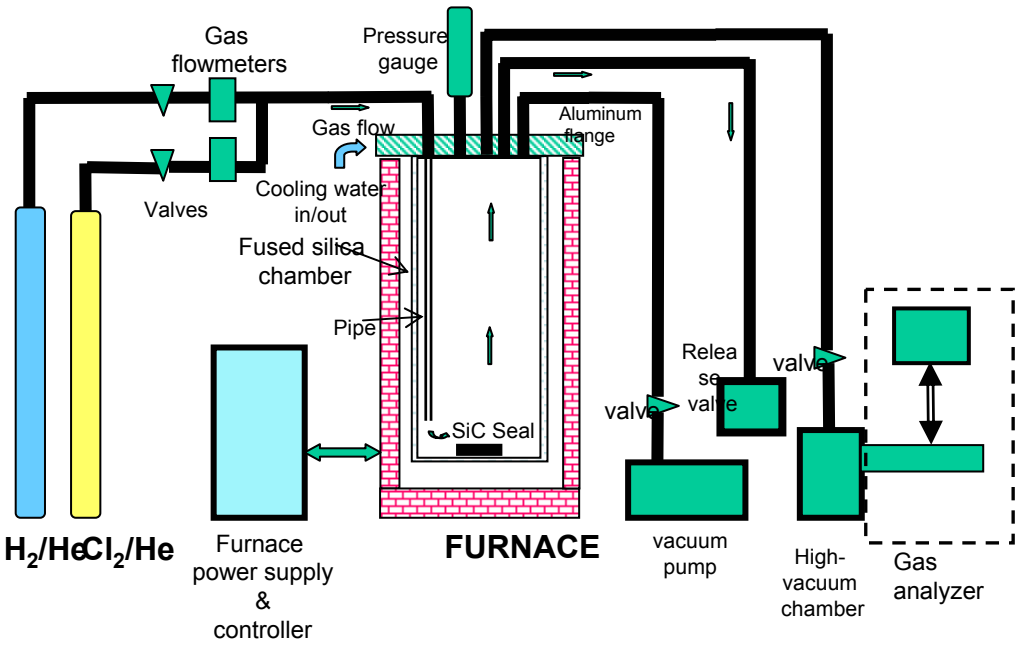




- **Two Milestones achieved:**
  - Coating of insulating seal
  - Coating of multiple seals simultaneously

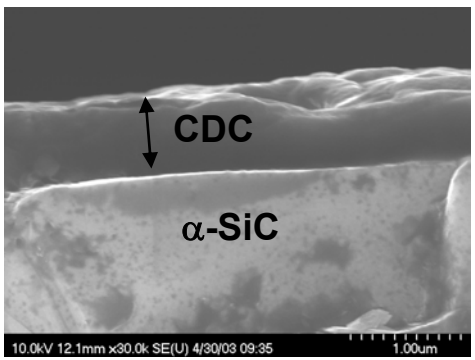
UNCD coatings meet uniformity and roughness specs

Carbide Derived Carbon (CDC) facility at ANL

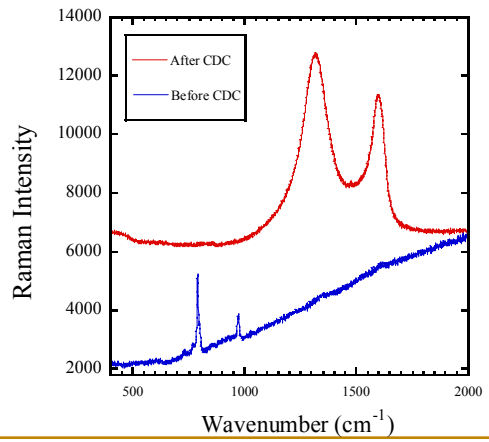


- **Milestone: Use CDC as seed layer for UNCD growth**
  - Improve adhesion
- **CDC: Selective Etching of Silicon from SiC in Cl_2/H_2**
- **Film structure, bonding (diamond vs. graphite) VERY sensitive to ratio of gas**
- **CDC films studied by XPS, SEM, RAMAN**
- **Two UNCD films successfully grown on CDC treated substrates**

Cross-section SEM



Raman data



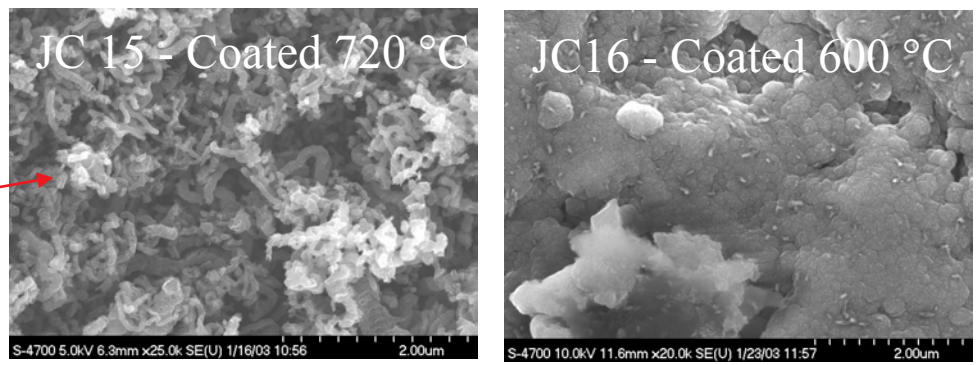
Future Work

- **Coat large numbers of seals for prototype testing at industrial facilities**
  - Film uniformity, waviness, smoothness, reproducibility of process
  - Friction, dry-running, thermal shock, etc.
  - Long-term tests
    - *Verification of value-added of UNCD coated seals*
- **Develop UNCD process for new seals**
  - New materials
  - New sizes/types/applications (high volume, engineered, gas seals, etc.)
- **Investigate CDC as seed layer for UNCD.**
  - Adhesion tests
  - Prototype testing

Hurdles to Overcome

- **Need NEW 11” IPLAS microwave plasma system**
  - Needed to meet FY04 milestones/deliverables
  - Needed to coat the numbers of seals for prototype testing at industrial facilities
  - Time-share available on upgraded 11” reactor (OBER funding)
- **Seal Materials vary a LOT!**
  - α-SiC at Crane NOT the same as Morgan, CoorsTek, etc.
  - Traces of impurities (especially Iron) a problem
    - *Need to develop process for each seal type?*
- **Delamination may be an issue for new material types**

Carbon Nanotubes!



Commercialization Pathway

- **Advanced Diamond Technologies, Inc. (www.thindiamond.com)**
  - founded by ANL & Uni. Of Chicago, to commercialize UNCD technology for all applications (Seals, MEMS, sensors, etc.)
- **Broader industrial participant base established**
  - John Crane, CoorsTek, Morgan AM&T, Advanced Diamond Technologies, Inc., Innovative Plasma Systems (IPLAS) GmbH
  - Types of seals, application areas driven by industrial partners
  - Testing of prototypes to be done at industrial facilities
  - $6.2M proposal written to OIT to scale-up and commercialize UNCD coatings on seals.
- **Economic analysis performed by ANL/ADT/Crane**
  - Need 11” reactor for engineered seals, 27” for high-volume